



1 analyte exposure will become uncertain under dynamically changing environmental conditions.  
2 Active sampling allows active flow of the air sample and can direct the flow through pneumatic  
3 tubing, valve(s), collection devices, and gas chromatographic columns prior to or down stream of  
4 the sensor. Active sampling draws sample past the polymer coated sensor, but does little to  
5 accelerate the sorption or desorption of the analyte molecules from the active surface of a chemical  
6 sensor.

7 Brief Summary of the Invention

8 Accordingly, it is an object of the present invention to provide a method and apparatus for  
9 delivering a sample of ambient air/gas to a chemical sensor resulting in accelerated signal  
10 kinetics.

11 It is a further object of the present invention to provide a method and apparatus for  
12 delivering a sample of ambient air to a chemical sensor wherein the interaction of molecules of an  
13 analyte in the gas sample with the surface of the sensor is maximized.

14 It is a further object of the present invention to provide a method and apparatus for  
15 delivering a sample of ambient air to a chemical sensor whereby the interaction of interfering  
16 molecules, such as water in the gas sample, with the surface of the chemical sensor can be  
17 minimized.

18 It is a further object of the present invention to provide a method and apparatus for  
19 delivering samples of ambient air to a chemical sensor whereby a baseline for the chemical sensor  
20 can be established between discrete samples.

1           It is a further object of the present invention to provide a pulsed gas sampling technique that  
2           increases the sorption rate of analyte into a sorbent coated chemical sensor by up to 3 orders of  
3           magnitude faster than conventional pneumatic gas sampling techniques that pump air over a sorbent  
4           film at atmospheric pressure.

5           It is a further object of the present invention to provide a pulsed gas sampling technique that  
6           allows rapid clean up of a sorbent coated sensor to a vapor-free state that allows the identification  
7           of an essentially analyte-free baseline.

8           These and other objects are attained by an apparatus for detecting the presence of at least one  
9           analyte in ambient air, the apparatus comprising

10           at least one sensing element comprising a surface having at least one sorbent coating, such  
11           as a chemoselective polymer coating, that selectively interacts with at least one analyte and  
12           provides a detector for detecting the selective interaction of the at least one chemoselective  
13           polymer with the analyte,

14           a housing that encloses an environment surrounding the at least one sensing element, the  
15           housing including an inlet port connected to a sampling pump for taking a gaseous sample from  
16           ambient air into the housing under reduced pressure, a valve or something similar for sealing the  
17           environment surrounding the sensing element so that the environment surrounding the at least one  
18           sensing element can be isolated from ambient air and evacuated, and an outlet port connected to the  
19           sampling pump under vacuum for removing the gaseous sample from the environment surrounding  
20           the at least one sensing element,

1 wherein the size and orientation of the inlet port are selected so that the gaseous sample is  
2 directed to strike each at least one sensing element in a turbulent flow that is substantially  
3 perpendicular to the surface of the sensing element having the chemoselective polymer.

4 These and other objects are further attained by a method of monitoring ambient air to detect  
5 the presence of an analyte, the method comprising the steps of

6 (a) providing an apparatus that comprises a sensing element comprising a surface having a  
7 sorbent polymer coating that selectively interacts with the analyte and means to detect the selective  
8 interaction of the sorbent coating with the analyte, a housing that encloses an environment  
9 surrounding the sensing element, the housing including an inlet port connected to a sampling pump  
10 for removing or collecting a gaseous sample from ambient air and taking the gaseous sample into  
11 the housing under pressure, wherein the size and orientation of the inlet port are selected so that the  
12 gaseous sample is directed to the sensing element in a turbulent flow that is substantially  
13 perpendicular to the surface having the sorbent coating, an outlet port for removing the gaseous  
14 sample from the environment surrounding the sensing element and means for sealing the  
15 environment surrounding the sensing element so that the environment surrounding the sensing  
16 element can be isolated from ambient air and evacuated,

17 (b) sealing the environment surrounding the sensing element from ambient air and evacuating  
18 the environment, so that a baseline for the sensing element is established,

19 (c) collecting a gaseous sample from ambient air and taking the gaseous sample into the  
20 housing initially under reduced pressure so that the gaseous sample is directed to strike the sensing

1 element in a turbulent flow that is substantially perpendicular to the surface having the  
2 chemoselective polymer coating, whereby molecules of the analyte, if present in the gaseous  
3 sample, interact with the chemoselective polymer and wherein any such interaction is detected, and  
4 whereby low molecular weight species not of interest in the gaseous sample are propelled by the  
5 turbulent flow towards the outlet port, and (d) repeating steps (b) - (c) to cyclically monitor the  
6 ambient gas for the presence of the analyte and restore the sensing element to its baseline.

7 Brief Description of the Drawings

8 Fig. 1 is a sketch of the first embodiment of the invention illustrating the evacuated gas  
9 sampling pneumatic system, or the basic embodiment, which has fast signal rise kinetics and a  
10 relatively slow recovery time.

11 Fig. 2 is a gas sampling/detect timing diagram for the basic embodiment of Fig. 1.

12 Fig. 3 is a sketch of the second embodiment of the invention illustrating the flush  
13 evacuated gas sampling pneumatic system, or the flush embodiment, which results in rapid signal  
14 kinetics during and after vapor exposure.

15 Fig. 4 is a sampling/detect timing diagram of the flush embodiment of Fig. 3.

16 Fig. 5 is a plot for a SAW sensor response showing fast signal response and relatively slow  
17 recovery kinetics by incorporating modulated pneumatics of the Fig. 1 basic embodiment.

18 Fig. 6 is a plot for a SAW sensor response showing fast signal response and recovery  
19 kinetics by incorporating pressure modulated pneumatics and flow through purging for the Fig. 3  
20 flush embodiment.

Detailed Description of the Preferred Embodiment

This invention provides a generic gas sampling technique for chemical sensors such, as the chemoselective polymer coated surface acoustic wave (SAW) devices, that allows for rapid equilibrated chemical sensor signal responses and recovery to baseline kinetics for relatively low volatility vapors such as chemical nerve and blister agents in the 1-2 second time domain or less. In addition, this invention allows a simple and rapid environmentally independent signal baseline restoration in less than about 2 seconds after vapor exposure, without the need for any consumable materials.

A pulsed pneumatic gas sampling technique of this invention reduces the sorption of water into polar polymers by up to 95%. One hypothesis of the mechanism is as follows: the water molecules have a molecular size that is comparable to oxygen and nitrogen molecules in the air and in a turbulent pneumatic flow path, the molecules become entrained in the air flow and are significantly prevented from sorbing to the polymer film that they flow past. Larger molecules of interest are less affected by the turbulent flow path and are readily sorbed to thin polymer films.

The apparatus of this invention can be used with any type of chemical sensor, including but not limited to a surface acoustic wave sensor (SAW), that has a chemoselective surface, that is, a sorbent coated or functionalized surface that selectively interacts with an analyte. Moreover, the invention is intended to include multiple sensors or arrays of sensors or sensors with surfaces having multiple coatings for detecting multiple analytes. Multiple sensors may share a common sampling pump and a common vacuum pump, but may have separate chambers with separate inlet ports and

1 outlet ports. In one such design, a sample of ambient air is pumped into a cubic structure having a  
2 chemical sensor on each of four faces of the cube, each sensor sharing a common sampling pump  
3 and vacuum pump, but having its own separate inlet and outlet.

4 In the apparatus of the invention, the surface of the chemical sensing element is enclosed or  
5 surrounded by a manifold or housing that allows the surface to be sealed off from the ambient  
6 environment and for the area surrounding the surface to be evacuated. Evacuation of the chamber  
7 surrounding the surface of the chemical sensing element removes volatile elements from the  
8 sorbent coating and the area surrounding it and allows for a baseline for the sensing element to be  
9 established. A pressure on the order of 10"-17" mercury will substantially remove or clean the  
10 surface of the sensing element where the element is 0.3" x 0.05", the inlet port is 0.1" directly  
11 below the tubular inlet port of 0.4" in diameter with the pump flow at 3 l/min. Evacuation to  
12 reduced pressure also increases the sorbency characteristics of the chemoselective polymer by  
13 removing any volatile molecules from the interior of the polymer. The housing includes an inlet port  
14 that is connected to a pump so that a gas sample taken from ambient air can be pumped into the  
15 chamber. The gas sample entering the chamber attains a high velocity and a turbulent flow due to  
16 the action of the pump and due to the release of the vacuum. The turbulent flow is directed by the  
17 placement of the inlet port relative to the surface of the sensing element so the gas sample strikes the  
18 surface of the sensing element in a substantially perpendicular manner with respect to the surface  
19 of the sensing element, as opposed to being directed in a substantially parallel direction to the  
20 surface. This dramatically increases the opportunity for and speed of interaction of any analytes of

1 the gas sample with the surface of the sensing element. ( The force of the turbulent flow carries small  
2 molecules, such as water molecules, that could potentially interfere with the response of the  
3 chemoselective polymer, away from the sensing element so that their interaction with the  
4 chemoselective polymer is minimized. ) As used herein, "substantially perpendicular" means non-  
5 parallel or at an angle and that the overall flow vector for the turbulent gas flow is perpendicular  
6 to the surface of the sensor element. Some deviation from perpendicular are acceptable.

7 After the gas sample has had sufficient time to interact with the chemoselective polymer so  
8 that molecules of the analyte, if present, can be detected, the inlet port is sealed off and the chamber  
9 surrounding the sensing element is evacuated to return the sensor to its baseline. The cycle is then  
10 repeated so that ambient air is monitored continuously over a period of time.

11 The interaction of an analyte with the chemoselective material of the sensing element  
12 generates a signal which can be monitored according to the type of sensing element.

13 Because of the faster signal kinetics, time of the sensing element of the present invention  
14 compared to conventional chemical sensors, it is now possible to use a chemical detector that  
15 operates with an orthogonal technology to sorbent material based detector with similar signal  
16 kinetics. The data from each of the two sensors can be merged and analyzed together.

17 A chemical transducer with a chemical interface such as a polymer coated SAW sensor, is  
18 operated under alternating pressure conditions from ambient to evacuated in a repeated cycle.  
19 Exposing the sensor, initially under reduced pressure, to ambient air rapidly draws analyte vapor  
20 into the sensor, accelerating and driving vapor molecules into the polymer film coated on top of the



1 SAW device. The SAW sensor frequency signal is monitored during the cyclical operations.  
2 Exposure to an uncalibrated nerve agent simulant dimethylmethylphosphonate (DMMP) vapor  
3 source for approximately 0.5 seconds, during the sensor exposure to ambient air results in a rapid  
4 response providing 90% of the total signal response within approximately 0.2 seconds. After the  
5 vapor source is removed, the signal recovery is accelerated by sweeping out relatively volatile  
6 vapors with a flow through purging step. Immediately following the flow through purging, the  
7 evacuation is applied first to remove the volatile species and then the flow through purging is used  
8 to remove the non-volatile species as they are "stickier" than the volatile species. An increase in  
9 signal response kinetics for chemical warfare agents of approximately 1-2 orders of magnitude can  
10 be established with the pressure modulated pneumatics.

11 In order to optimize the signal response and recovery kinetics, a pneumatic configuration  
12 shown in Fig. 3 was designed, with a timing diagram shown in Fig. 4. Recovery time of the Fig. 3  
13 flush embodiment as compared to the Fig. 1 basic embodiment is greater than about 4 times, i.e.,  
14 recovery time for the basic embodiment shown in Fig. 1 is typically 3-5 seconds and that for the Fig.  
15 3 flush embodiment is typically less than 1 second. The cause and effect of various events during  
16 a typical cycle with the flush embodiment shown in Fig. 3 is illustrated in Fig. 4. Data collected  
17 for a DMMP exposure to a SAW sensor coated with a chemoselective polymer (NRL polymer AD1)  
18 is shown in Figs. 5 and 6 for pneumatics with and without the purge flow through prior to  
19 applying evacuation. The rapid signal recovery kinetics observed with the application of flow  
20 through purging prior to evacuation is exemplified in Fig. 6 for the flush embodiment shown in Fig.

1 3. Signal response to 90% of the maximum signal is approximately 1 second as before, and the  
2 signal recovery to baseline is dramatically reduced to approximately 2 seconds for DMMP, a  
3 precursor for nerve agent manufacture and a nerve agent simulant.

4 Referring to the drawings, Fig.1 is a sketch of the basic embodiment 100 of the invention.  
5 This basic embodiment includes 2-way valve 102 through which a gas sample of the ambient air  
6 is introduced through line 104; and then through line 106; through sensor housing 108 having inlet  
7 port, outlet port and a sensing element; through line 110; into pump 112; and out through exhaust  
8 line 114. The pump provides the suction to draw in the gas sample from the ambient air.

9 Operation of the basic embodiment of Fig. 1 can be more easily described by reference to  
10 the timing diagram depicted in Fig. 2 which shows one period, duration of which can vary  
11 depending on the many variables of the system. As Fig. 2 shows, pump 112 is on during the entire  
12 period and draws in the gaseous sample during the time valve 102 is open. Detection of the analyte  
13 by the sensing element is also made during this time.

14 The time period required for identifying a clean baseline varies in time length depending on  
15 pumping properties and exact pneumatic configuration. For embodiments of Figs. 1 and 3, the time  
16 typically varies between about 0.05 to 10 seconds.

17 Fig. 3 is a sketch of the flush embodiment of the sensor system 300 which draws in a gaseous  
18 sample of the ambient air through line 312. The ambient air can contain an analyte or gas which is  
19 desired to be removed. The ambient air can contain more than one analyte. The sample proceeds  
20 through 3-way valve 314 which then proceeds through line 316 to sensor housing 318 which

1 contains an inlet port, an outlet port and one or more sensing elements which have a chemoselective  
2 material thereon. There may be more than one sensing element each covered with a different  
3 chemoselective material which interacts with different analytes or there can be a single sensing  
4 element coated with one or more different chemoselective materials for detecting presence of  
5 different analytes. Neither the sensing element nor the inlet or outlet ports are shown. The inlet port  
6 is arranged so that it delivers the sample in a turbulent flow that is directed at an angle or is  
7 substantially perpendicular to the sensing element.

8 A tubular inlet port 0.4" in ID with the sensing element spaced from the inlet by 0.1"  
9 at a flow rate of 3 l/min, can produce turbulent flow above the sensing element. Laminar flow can  
10 be obtained with the same arrangement but with inlet port at 0.5" ID.

11 From sensor housing 318 through exit port, the sample is conveyed through line 322 to  
12 pump 324. Pump 324 provides some impetus for drawing the sample against the sensing element.  
13 Pump 324 is adapted to convey gas through line 326 to 3-way valve 328 where the gas, or any part  
14 thereof, can be exhausted through line 330 or conveyed further through line 332 to scrubber 334.

15 When moving through the scrubber, the air is stripped of analyte or cleaned and this scrubbed gas  
16 is used to restore the baseline condition by flowing it over the sensing element, as will be described.

17 After the gas is cleaned by stripping it in scrubber 334, it is conveyed through line 336 to 2-  
18 way valve 338, line 340, reservoir line 341, line 343, 2-way valve 342, line 344 and to valve 314.

19 Line 336, valve 338 and line 340, reservoir line 341, line 343, valve 342 and line 344 form  
20 a reservoir for scrubbed gas, which is typically the gas sample or any part thereof.

1           The flush embodiment of Fig. 3 is designed to restore baseline condition of the sensing  
2 element with the scrubbed gas, as is explained below.

3           Operation of the flush embodiment of Fig 3 can be more easily understood by reference to  
4 Fig 4, which is the timing diagram of the Fig. 3 embodiment. The cycle times given in Fig. 4 are  
5 merely illustrative and are not typical of the actual times. Referring to Fig. 4, partial evacuation cycle  
6 400, i.e., the first cycle, is shown at the top and designates the cycle during which lines 312, 344 and  
7 332 are closed off and pump 324 is on and exhausts all gases from valve 314, line 316, sensor  
8 housing 318 with its inlet and outlet ports and the sensing element, line 322, valve 328 and line 326  
9 through exhaust line 330. As Fig. 4 indicates, duration of this cycle is 5 seconds and it provides a  
10 vacuum or low pressure, i.e., below atmospheric, over the sensing element. This condition can also  
11 be described as having valve 314 on and pump 324 also on, the pump providing the evacuation draw.

12           The next or the second cycle also has duration of 5 seconds and it is designated as complete  
13 evacuation or removal cycle 402 during which, lines 312 and 330 are closed and line 344 is opened  
14 so that gas can circulate in the closed system, with pump 324 on, through valve 314, line 316,  
15 sensor housing 318, line 322, line 326, valve 328, line 332, scrubber 334, line 336, valve 338, line  
16 340, reservoir line 341, line 343, valve 342 and line 344, with line 312 being closed. The purpose  
17 of this cycle is to advance scrubbed reservoir gas against the sensing element in order to reset  
18 baseline condition thereof. This cycle results in a gas pressure over the sensing element that is higher  
19 than in the partial evacuation cycle but lower than atmospheric, assuming that the ambient air is at  
20 atmospheric pressure. At the commencement of this second cycle, since gas pressure over the

1 sensing element is lower than that of the reservoir gas, this pressure differential is relied on to draw  
2 the reservoir gas in. As the reservoir gas, i.e., essentially from reservoir line 341, rushes in over the  
3 sensing element due to the pressure differential, it strips off analyte molecules from the sensing  
4 element to restore the sensing element to its baseline condition. This is made possible by the fact that  
5 the pressure over the sensing element is lower than the pressure of the reservoir gas thus creating a  
6 pressure differential for drawing in the reservoir gas. The other fact which makes possible restoration  
7 of the baseline condition is that the reservoir gas has been scrubbed of analyte. This cycle can also  
8 be described as the time both valve 314 and pump 328 are on. The second cycle can also be  
9 described as having valves 342 and 328 on.

10 The next or the third cycle is the sampling cycle 404, designated as prior sampling, during  
11 which line 312 is closed and line 332 is opened so that there is passage through valve 314; line  
12 316; sensor housing 318 with inlet port, outlet port and the sensing element; line 322; pump  
13 324; and out through line 330. The purpose of this third cycle, duration of which is 5 seconds, is  
14 to replenish the reservoir gas against the sensing element. As should be apparent, although the  
15 third cycle is designated as being prior sampling, no sampling of the ambient air is made.

16 The last or the fourth cycle 406, shown in Fig. 4, is designated as being sampling, and it does  
17 sample the ambient air. During this cycle, lines 344 and 332 are closed and line 312 is opened by  
18 virtue of manipulating valve 314 so that ambient air flows through line 312, valve 314, line 316,  
19 sensor housing 318, line 322, pump 324, line 326, valve 328, and out through line 330. The  
20 pressure differential between ambient air, which is typically atmospheric, and the pressure of the

1 sensor housing, which is typically sub-atmospheric, provides partial impetus for drawing the  
2 ambient air in. The pressure differential is typically sufficient to draw in less than about one-half,  
3 and typically about one-third, of the gaseous sample that is tested, with remainder being drawn in  
4 by pump 328 which is turned on when the reservoir gas pressure and the pressure of the ambient air  
5 approximately equalize. In Fig. 4, portion of the ambient air that is drawn in by the pressure  
6 differential is denoted as 408 and the portion drawn in by pump 328 is denoted as 410.

7 Reservoir line 341 is typically 1/4" ID and 5' long and the other lines are typically short and  
8 are 1/8"-1/4" ID tubing. The reservoir section, which includes line 336, valve 338, line 340,  
9 reservoir line 341, line 343, line 342 and line 344, but essentially line 341 since volume of the other  
10 lines is small because they are typically short, acts as a reservoir of scrubbed gas for the system  
11 during the complete evacuation cycle when the scrubbed gas is introduced against the sensing  
12 element when the baseline condition of the sensing element is reestablished by removing analyte  
13 from the sensing element by the flowing scrubbed gas.

14 Because the baseline can be reset in a rapid fashion and in a repeated manner, if there are any  
15 environmental signal response drift issues, these can be readily nullified because the baseline can  
16 be reset in less than about two seconds. Hence, temperature and humidity sensor signal drift  
17 issues are effectively eliminated.

18 Also, because of the very fast signal kinetics, the polymer coated SAW sensors are now  
19 comparable in kinetics to a chemical detector based on an orthogonal technology, such as the ion  
20 mobility spectrometer (IMS), which uses a direct vapor inlet, and not a membrane, or generally,

1 a fast signal kinetic chemical detector based on an orthogonal detection technology , such as the  
2 IMS . Joining the two technologies together is important since it is of no use if one sensor is much  
3 faster in terms of responding to a gas because the fusion of any data or any signal processing  
4 algorithm becomes complicated and the fast sensor has to wait for the slow sensor to catch up.

#### 5 Examples

6 An array of four -250 MHz SAW chemical sensors (each separately coated with a thickness  
7 of approximately 50 nm of the NRL polymers CSP2, T1, AD1, and EH1 corresponding to 250KHz  
8 frequency shift before and after coating) were pneumatically connected in parallel configuration to  
9 a miniature TD-4x2NA Brailsford pump, and miniature 2-way valve as shown in Fig. 1 The  
10 pneumatics were operated with a repeated cycle that incorporated two main operations. 1. The  
11 sensor was evacuated (valve closed) by operating the pump to reduce the pressure within the sensor  
12 chamber and thereby remove air, and vapors in the pneumatics contained between the pump, sensor,  
13 and valve 2. Turning the pump off and switching the valve to the open position, to allow ambient  
14 air with an analyte dimethylmethylphosphonate (DMMP) vapor to rush into the pneumatics and  
15 the sensor array. Operations 1 & 2 were repeated in a continuous cycle, where operation 1 was  
16 maintained for a period of 5 seconds, and operation 2 was maintained for a period of 5 seconds. The  
17 cycle events are detailed in Fig. 2.

18 The following results were observed: exposing the sensor, initially under reduced pressure,  
19 to ambient air to rapidly draw analyte vapor into the sensor, accelerating and driving vapor  
20 molecules into the polymer film coated on top of the SAW device. The SAW sensor frequency signal

1 was monitored during the cyclical operations 1 & 2 described above. Exposure to an uncalibrated  
2 DMMP vapor source for approximately 0.5 seconds, during operation 2, resulted in a rapid  
3 response providing 90% of the total signal response within approximately 0.2 of a second. The  
4 maximum responses were 35 KHz, 31KHz, 26KHz, and 6KHz of signal for SAW devices coated  
5 with polymers EH1, T1, AD1, and CSP2 respectively. After the vapor source was removed, the  
6 signal recovery to baseline took an extended period of time of between 10 and 60 seconds,  
7 depending on the polymer. The corresponding signal response after 0.7 seconds from the identical  
8 SAW sensor coated with polymer EH1 and challenged with the same vapor challenge for "normal"  
9 vapor sampling (-continuous stream of the vapor pumped over the sensor at a constant pressure)  
10 produced a much slower signal response of 1000Hz.

11 In order to improve the recovery of the SAW chemical sensor after vapor exposure, the  
12 evacuated stage was preceded by a continuous flow stream to remove volatile species from the  
13 sensor. Subsequent evacuation removed less volatile vapor components. This operation of baseline  
14 recovery allows a stepwise recovery to a clean vapor free baseline signal. In order to optimize the  
15 signal recovery kinetics, a redesigned pneumatic configuration was used as shown in Fig. 3, with  
16 a timing diagram shown in Fig. 4. Data collected for a DMMP exposure to a SAW sensor coated  
17 with NRL polymer Adiol is shown in Figs. 5 and 6. The rapid signal recovery kinetics observed  
18 with the application of flow through purging prior to evacuation is exemplified in Fig. 6. Signal  
19 response to 90% of the maximum signal is approximately 1 second as before, and the signal recovery  
20 to baseline is dramatically reduced to approximately 2 seconds for dimethylmethylphosphonate



1 (DMMP), a precursor to nerve agents and a nerve agent stimulant.

2 In addition to DMMP tests, toluene and dinitrotoluene exposure tests were carried out to  
3 evaluate the sampling technique for its effectiveness for more volatile and less volatile species.  
4 Responses to more volatile species, such as toluene, were reduced.

5 Obviously, many modifications and variations of the present invention are possible in light  
6 of the above teachings. It is therefore to be understood that, within the scope of the appended claims,  
7 the invention may be practiced otherwise than as specifically described.